

Sorption Properties of Chitosan in the Refining of Rough Indium

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Abstract

The degree of purity of cathode deposits during the electrochemical refining of rough indium depends on the content of impurity metals in the electrolyte. In this work, an additional sorption purification of the refining electrolyte was carried out in order to reduce the content of such impurity metals as cadmium, lead, copper. Chitosan was used as a sorbent due to high sorption properties with respect to heavy metal ions. The determination of the concentration of the studied metals before and after the sorption was carried out by the method of differential pulse anodic stripping voltammetry (DPASV). The experimental results allowed to calculate the amount of metal sorbed by chitosan and the efficiency of its removal. The Langmuir and Freundlich adsorption models were applied to describe the equilibrium isotherms and isotherm constants were determined. The Langmuir model agrees very well with experimental data. An inductively coupled plasma optical emission spectroscopy (ICP-OES) method was used to determine the presence of impurity metals and the degree of purity of electrorefined indium. The use of chitosan as a sorbent in the purification of rough indium allows to reduce the concentration of impurity metals in cathode deposits and to increase the content of the base metal to 99.9994%.

1. Introduction

Practical application of indium in the space, nuclear, aviation industry, in the production of liquid crystal screens, photocells and in microelectronics is due to its properties such as strength, plasticity, corrosion resistance. These properties are inherent only to indium of high purity. Existing technologies for obtaining high-purity indium are multi-stage and require the use of combined methods. Electrolysis is a universal method for purifying metals from metallic and non-metallic impurities, characterized by high productivity and the ability to automate the process. In electrorefining of indium, the removal of impurity metals by traditional methods often leads to an insufficient reduction in their concentration. Therefore, one of the promising directions in the refining of metals is the use of the electrochemical method in combination with others [1–3].

There is a continuous purification of the electrolyte from the impurities accumulating during the electrolysis, including the sorption stage, i.e. passing the solution through the layer of activated carbon and ion exchange resin [4]. To purify the copper refining electrolyte, three types of sorbent were proposed in [5]: activated carbon, zeolite and chelate resin, of which the third proved to be very effective.

The main requirements for the sorbent when used in the electrorefining of metals are chemical purity, stability, high sorption characteristics with respect to impurities. As a sorbent that meets these requirements, we have chosen a chitosan – deacetylated chitin derivative that exhibits high sorption properties when heavy metal ions are removed in industrial wastewater [6].

The purpose of this work is to use the sorption properties of chitosan in the purification of indium produced in Kazakhstan at the Ust-Kamenogorsk enterprise of KazTsink JSC.

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Atomic absorption spectroscopy, electrochemical methods of analysis, optical emission and mass spectrometry with inductively coupled plasma (ICP-OES, ICP-MS) are widely used in the study of sorption characteristics of sorbents [7]. Methods of differential pulse anodic stripping voltammetry are often used in the analysis to determine trace amounts of substances because of their high sensitivity and selectivity [8]. In connection with this, differential pulse voltammetry (DPV) was used in this research to study the sorption properties of chitosan. In order to increase the selectivity, sensitivity and efficiency of the determination of small contents of impurity metals in the indium refining electrolyte, we used a modification of the surface of the glassy carbon electrode with a thin layer of metallic mercury.

2. Experimental

The voltammograms were recorded in a differential-pulse regime using the potentiostat-galvanostat Metrohm Autolab. The working electrode was a mercury-film glassy carbon rotating disc electrode, the auxiliary electrode was a platinum plate. All potentials were measured relative to the reference electrode Ag/AgCl (3.5M KCl). Electrochemical deposition of mercury on the surface of the glassy carbon electrode was carried out in accordance with GOST standard P 51301-99 (ex-situ) [9].

Concentration of impurity metals (copper, lead, cadmium) was carried out from standard solutions (GSO) in the concentration range 10^{-7} M – 10^{-5} M. The supporting electrolyte was 1 M sodium chloride solution. The pH of the solutions (~ 2) was created by acidification with HCl (37%) of Sigma Aldrich. Before each measurement, the electrolyte was purged with argon for 5 min. Concentrating was carried out at more negative values than the potentials of the peaks. The rest period of solution was 15 s, the pulse amplitude was 50 mV and the scan rate was 10 mV/s. All experiments were performed at 25 °C.

The sorbent was the chitosan of Sigma Aldrich. The equilibrium sorption of Cu^{2+} , Pb^{2+} , and Cd^{2+} ions was carried out by contacting 0.1 g of chitosan with 200 ml of a solution containing metal ions in a concentration range of 10^{-5} M – 10^{-4} M in conical flasks for 90 min on a shaker. The mixture was filtered and the filtrate was analyzed for the content of metal ions by the calibration graph from the results of differential pulse voltammograms.

3. Results and discussion

To determine the small concentrations of impurity metals in the refining electrolyte, the differential pulse voltammetry (DPV) method was used. The detection limits for DPV are about 10^{-10} – 10^{-9} M, while for irreversible systems the loss in sensitivity is not so great [10].

In comparison with traditional static mercury drop electrodes on film electrodes, during the anodic stripping voltammetric analysis, higher sensitivity and better resolution of the peaks are achieved. The sensitivity of the determination depends on the thickness of the film, i.e. the amount of deposited mercury.

Initially, anodic voltammograms of standard solutions of copper, lead and cadmium, shown in Fig. 1, were obtained for the construction of calibration curves. The insertion graphs show the calibration curves of the peak current values of the electro-oxidation of the studied metals from their concentration in the electrolyte.

Determination of the content of metal ions by the method of anodic stripping voltammetry is based on the dissolution of the concentrate from the anode, which leads to the appearance of a current peak whose height depends on the concentration of the metal in the amalgam. As can be seen from Fig. 2, the current values of the anode peak (i_p) increase with the increasing concentration of metal ions.

The height of the peak on the differential pulse voltammogram is directly proportional to the concentration of the electroactive substance c_a and depends, among other factors, on the pulse amplitude E_A and the pulse duration t_p .

In stripping voltammetry, the Randles-Shevchik equation is used [11]:

$$I_p = k \cdot n^{3/2} \cdot A \cdot D_{Me^0(Hg)}^{1/2} \cdot C_{Me^0(Hg)} \cdot \nu^{1/2} \quad (1)$$

where, n – number of electrons, A – surface area of the electrode, $C_{Me^0(Hg)}$ – the diffusion coefficient of the determining substance in the amalgam, $C_{Me^0(Hg)}$ – concentration of the determining substance in the amalgam, ν – scan rate.

When a thin mercury film electrode (TMFE) is used, the peak current is proportional to the scan rate ν and depends on the surface area of the mercury film A_F and the metal concentration in it at time of electrolysis t_e .

$$I_p = k \cdot n^2 \cdot A_F \cdot \nu \cdot t_e \cdot C_{Me^0(Hg)} \quad (2)$$

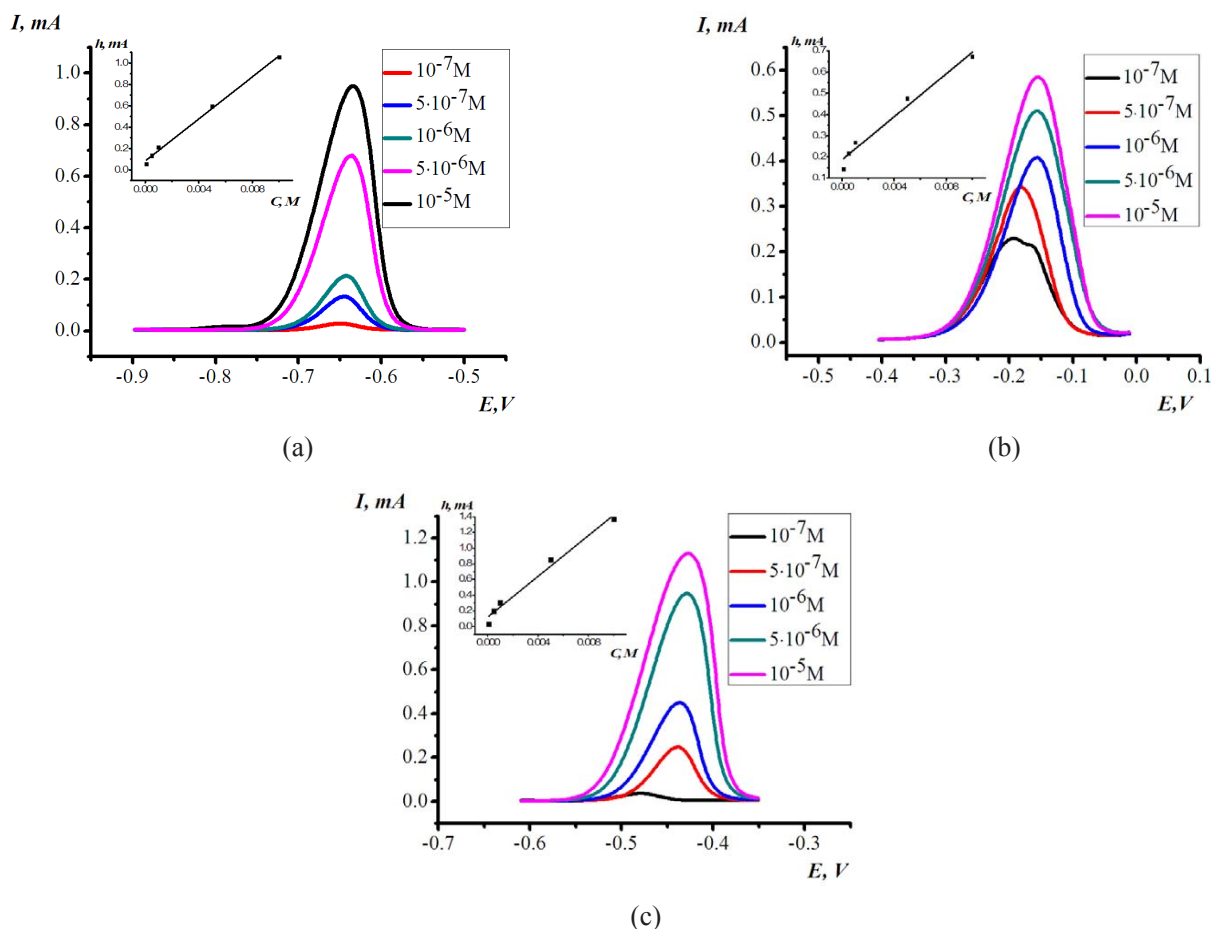


Fig. 1. Voltammograms obtained in DPV mode for different concentrations of the metallic species: (a) – Cd^{2+} ; (b) – Cu^{2+} ; (c) – Pb^{2+} and the respective calibration curves. The scan rate is 10 mV/s, the pulse amplitude is 50 mV, $t_{dep} = 5$ min, $r = 2.000$ rpm.

As a sorbent, chitosan is used in the work, which possesses high sorption properties in relation to the studied metals, chemical stability, ecological safety and ease of regeneration. The determination of the equilibrium concentration of the studied ions before and after the sorption of metals was carried out by the DPASV method [12]. The experimental results are shown in Fig. 2, from which a significant decrease in the content of impurity metals in the electrolyte is evident.

The results obtained allowed calculating the amount of sorbed metal and the efficiency of its removal using the following equation [13]:

$$Q = \frac{v(C_i - C_e)}{W} \quad (3)$$

where, Q – the amount of substance sorbed from the solution, v – volume of sorbate, C_i – concentration before sorption, C_e – concentration after sorption and W – mass of sorbent.

$$Sorption = \frac{C_i - C_e}{C_i} \cdot 100\% \quad (4)$$

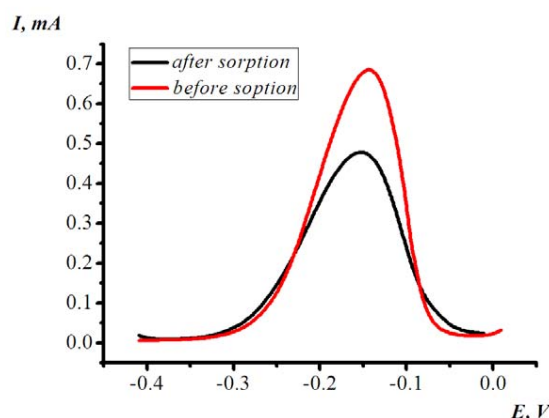


Fig. 2. Voltammograms obtained in DPV mode before and after sorption by chitosan for $2 \cdot 10^{-5} M Cu^{2+}$ solution.

The calculated values are given in Table 1. The experimental results were simulated using simple adsorption isotherms, such as the classical Langmuir and Freundlich equations [14, 15]. In addition to these equations, we also apply the Temkin and Dubinin-Radushkevich equations for interpreting experimental data on adsorption.

Table 1
Indicators of sorption of metal ions by chitosan

| Ions | Cd ²⁺ | | Cu ²⁺ | | Pb ²⁺ | |
|------|---|---------|------------------|---------|------------------|---------|
| | C _i , 10 ⁻⁵ mol/l | Q, mg/g | Sorption, % | Q, mg/g | Sorption, % | Q, mg/g |
| 1 | 0.212 | 9.43 | 0.822 | 63.38 | 0.994 | 23.99 |
| 2 | 0.936 | 11.92 | 1.61 | 64.72 | 4.188 | 50.53 |
| 4 | 5.168 | 57.47 | 3.906 | 76.89 | 10.94 | 66.0 |
| 6 | 9.288 | 68.86 | 6.18 | 80.00 | 18.98 | 76.3 |
| 8 | 13.964 | 77.65 | 8.128 | 81.1 | 26.522 | 80.0 |

3.1. The Langmuir model

The equation of the adsorption isotherm of Langmuir expresses the ratio between the amount of adsorption Q_e (mol/kg) and the equilibrium concentration of adsorbate in the liquid phase C_e (mol/m³):

$$Q_e = \frac{Q_0 \cdot K_L C_e}{1 + K_L \cdot C_e} \quad (5)$$

The equation constants were calculated from the slope and intersection of lines on the graphs in the corresponding coordinates of the linear Eq. (6): $1/Q_e$ from $1/C_e$ (Fig. 3).

$$\frac{1}{Q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 K_L C_e} \quad (6)$$

where C_e is the equilibrium concentration of adsorbate (mg/l), Q_e is the amount of adsorbed metal per gram of adsorbent at equilibrium (mg/g). Q_0 is the maximum monolayer capacity (mg/g), K_L is the Langmuir isotherm constant (L/mg).

3.2. The Freundlich model

The Freundlich adsorption isotherm is usually used to describe the adsorption characteristics of a heterogeneous surface [16]. Since the adsorption centers in this model have different energy values, first of all, the active sorption centers with maximum energy are filled. These data often correspond to the empirical equation proposed by Freundlich:

$$Q_e = K_f C_e^{1/n} \quad (7)$$

where K_f – the equilibrium constant of the Freundlich equation (mg/g), n – the adsorption intensity;

C_e – the equilibrium concentration of adsorbate (mg/l), Q_e – the amount of adsorbed metal per gram of adsorbent at equilibrium (mg/g).

Figure 4 presents experimental data on the adsorption of cadmium, copper, and lead by chitosan in the coordinates of the linear Freundlich equation $\log Q_e$ from $\log C_e$:

$$\log Q_e = \log K_f + 1/n \log C_e \quad (8)$$

The equilibrium constants were calculated from the slope and intersection of lines with the ordinate axis on the graph in the coordinates of Eq. (7). The parameters K_f and $1/n$ of Eq. (6), found graphically, allow us to find the adsorption equation, on the basis of which it is possible to calculate the number of adsorbed ions from the solution after adsorption under equilibrium conditions.

For adsorption of cadmium, copper and lead by chitosan, the Freundlich equation looks as follows:

$$Q_e = 0.714 \cdot C_e^{0.93}$$

$$Q_e = 1.259 \cdot C_e^{1.81}$$

$$Q_e = 1.224 \cdot C_e^{4.31}$$

The experimental results cannot be described by Temkin and Dubinin-Radushkevich isotherms, because of the small values of the correlation coefficients.

Table 2 shows the parameters of the Langmuir and Freundlich equations calculated graphically.

Comparison of the table data shows that the sorption of Cd²⁺, Cu²⁺, Pb²⁺ ions by chitosan is best described by the Langmuir model (the largest R²). This indicates that the sorption of the studied metals satisfies the boundary conditions for the applicability of the Langmuir model with a monomolecular coating.

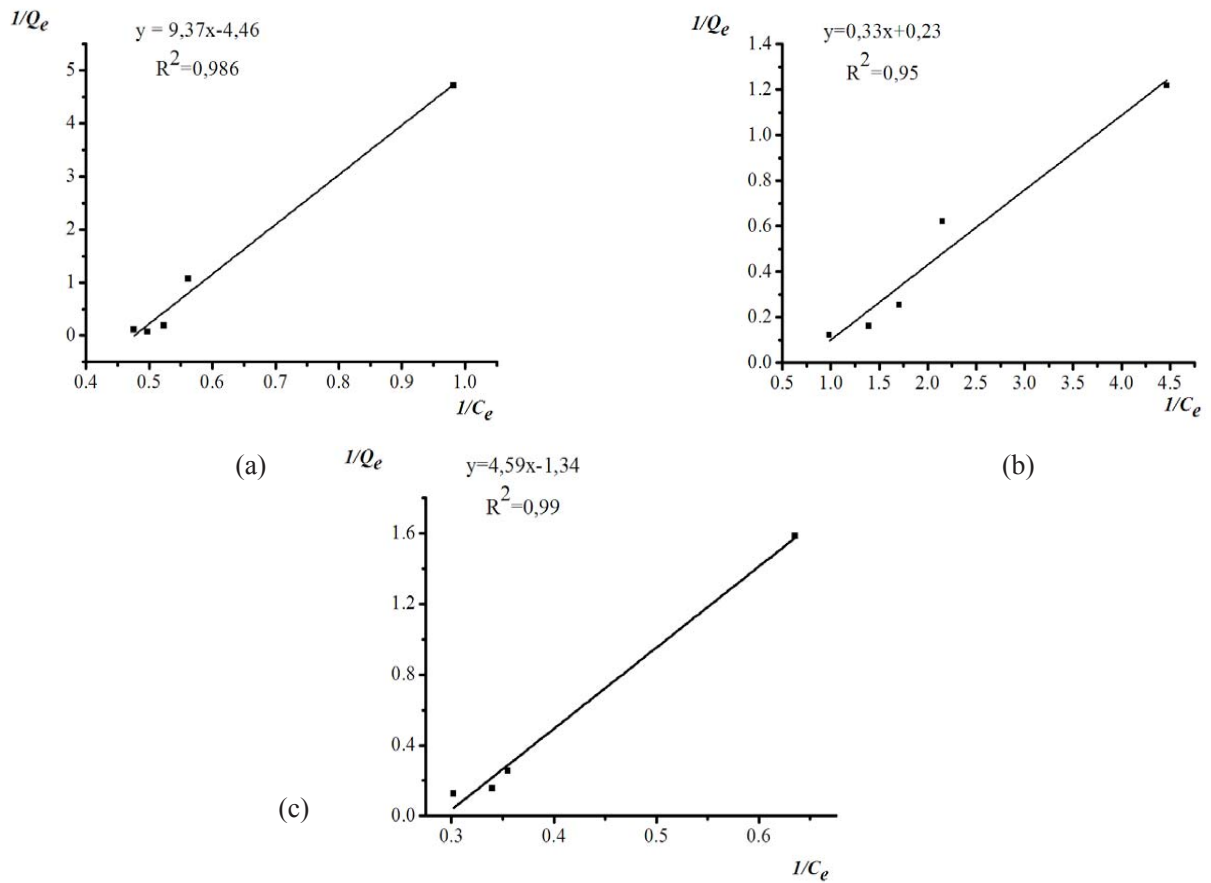
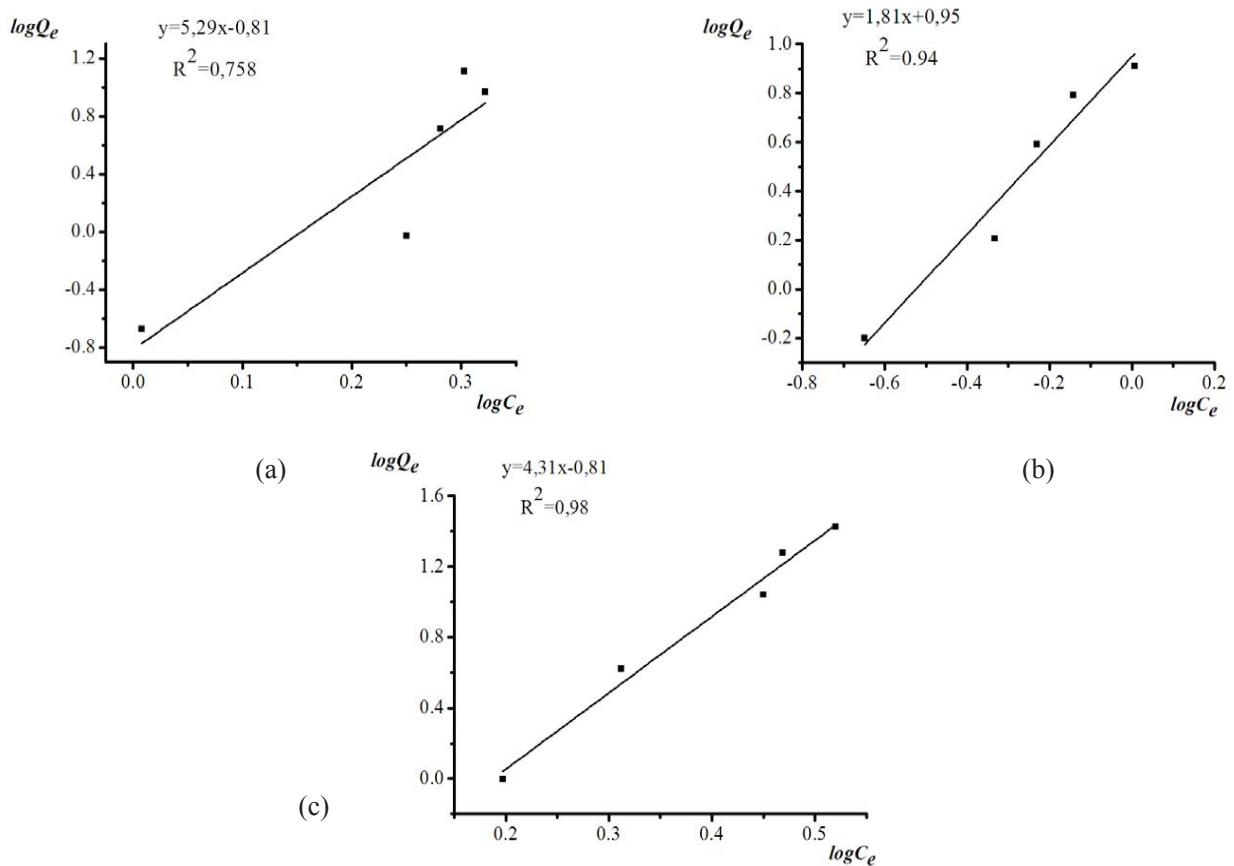
Fig. 3. Langmuir adsorption isotherms: (a) – Cd^{2+} ; (b) – Cu^{2+} ; (c) – Pb^{2+} .Fig. 4. Freundlich adsorption isotherms: (a) – Cd^{2+} ; (b) – Cu^{2+} ; (c) – Pb^{2+} .

Table 2
Langmuir, Freundlich isotherm constants for the adsorption of Cd²⁺, Cu²⁺, Pb²⁺ ions onto chitosan

| Metal ions | Langmuir isotherm | | | | Freundlich isotherm | | | |
|------------------|-----------------------|-----------------------|----------------|----------------|---------------------|-------|-----------------------|-----------------|
| | Q ₀ , mg/g | K _L , L/mg | R _L | R ² | $\frac{1}{n}$ | n | K _f , mg/g | R ²⁺ |
| Cd ²⁺ | 2.353 | 0.109 | 0.890 | 0.99 | 0.931 | 1.08 | 0.714 | 0.76 |
| Cu ²⁺ | 8.433 | 3.044 | 0.057-0.254 | 0.95 | 1.810 | 0.552 | 1.259 | 0.95 |
| Pb ²⁺ | 8.333 | 0.235 | 0.17-0.40 | 0.99 | 4.314 | 0.232 | 1.224 | 0.98 |

3.3. Electrolysis

Electrodeposition of indium was carried out in chloride electrolytes at an indium chloride concentration of 0.5 mol/l and a current density of 30 mA/cm². The choice of conditions for conducting electrolysis was carried out on the basis of previous works [17, 18]. The anode served as a rough indium, and the cathode was a titanium plate. The sorbent was located in a polymer partition separating the cathode and anode spaces. Scheme of the electrolysis installation is shown in Fig. 5.

The content of impurity metals in the obtained pure indium samples was determined by the ICP-OES method. Samples of solutions of indium cathode sediments were prepared for analysis as follows: after electrolysis, samples of electrodeposited indium were dissolved in nitric acid (osm) and diluted with bidistilled water to a certain volume. The results of the analysis are presented in Table 3.

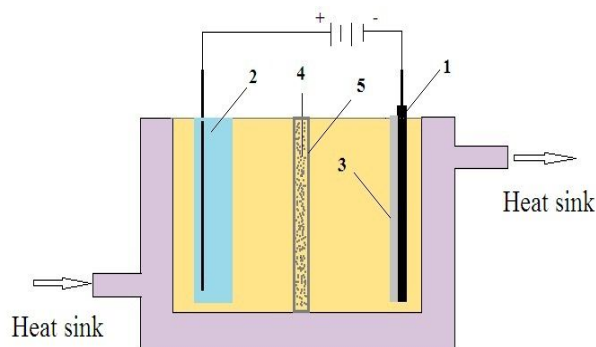


Fig. 5. Electrolysis installation: 1 – titanium cathode; 2 – rough indium anode; 3 – deposited indium; 4 – chitosan; 5 – polymeric partition.

The content of impurity metals in the cathode deposits decreases and leads to an increase in the purity of indium. The obtained results allow us to recommend chitosan as an effective sorbent of impurity metals of electrolyte during refining of other metals.

Table 3
Impurity metals and indium content in the cathode deposit

| Me | The composition of cathode deposits, * 10 ⁻³ wt% | | | |
|---|---|------------------------------------|--|---|
| | Rough indium | After electrolysis without sorbent | After electrolysis with sorbent (m = 0.0057 g) | After electrolysis with the sorbent (m = 0.026 g) |
| Cd | 1.0 | 0.048 ± 0.002 | 0.022 ± 0.001 | 0.011 ± 0.001 |
| Cu | 1.0 | 0.077 ± 0.004 | 0.035 ± 0.002 | 0.022 ± 0.001 |
| Fe | 1.0 | 0.769 ± 0.004 | 0.649 ± 0.032 | 0.361 ± 0.018 |
| Ni | 1.0 | - | - | - |
| Pb | 1.0 | 1.107 ± 0.055 | 0.649 ± 0.032 | 0.217 ± 0.011 |
| Tl | 1.0 | - | - | - |
| Zn | 3.0 | 0.029 ± 0.001 | - | - |
| Sn | 1.0 | 0.009 ± 0.001 | 0.007 ± 0.001 | 0.00090 ± 0.0001 |
| Indium content, wt% | | | | |
| In | 99.98 | 99.9979 | 99.9986 | 99.9994 |
| “-” means that the metal content is below the detection limit (30 µg/L) | | | | |

4. Conclusions

The sorption properties of chitosan in chloride electrolytes containing ions of cadmium, copper and lead have been studied. The content of the studied metals was determined before and after sorption by the DPASV method. The amount of sorbed metal and the removal efficiency were calculated for all the studied impurities.

The experimental results were simulated using the Langmuir and Freundlich sorption isotherms, from which the highest regression value corresponding to the Langmuir model.

Electro refining of rough indium with the use of chitosan as a sorbent was carried out. The results of the analysis indicate a significant decrease of the content of the studied impurity metals in cathode deposits. Thus, chitosan is an effective sorbent for reducing the content of cadmium, copper and lead ions in the indium refining electrolyte.

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